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Structural, reactivity and optical Properties of Homo- and Hetero- Binuclear CycloPlatinated(II) Complexes with bridging cyanide

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Coordination driven self-assembly and metallophillic ineractions provide power tools to construct bi- tri-or extended supramolecular luminescent structures featuring different and rich excited states with application in different fields([1]). Herein, we present a series of homonuclear and heteronuclear cycloplatinated(II) complexes featuring cyanide ligand. Homobinuclear symetrical $(NBu_4)[Pt_2(C\hat{}N)_2(p\text{-}MeC_6H_4)_2(\mu\text{-}CN)]$ were prepared by reaction of the corresponding mononuclear anionic complexes $Q[Pt(C\hat{}N)(p\text{-}MeC_6H_4)(CN)]$ ($C\hat{}N$ = bzq, ppy, dfppy) with $[Pt(C\hat{}N)(p\text{-}MeC_6H_4)(SMe_2)]$ ([2]). By contrast, neutralization reactions with one equivalent of $TlPF_6$ provides heteronuclear Pt-Tl compounds in excellent yield. Their structures were confirmed by single crystal X-ray diffraction and, as illustration, the structures of $(NBu_4)[Pt_2(dfppy)_2(p\text{-}MeC_6H_4)_2(\mu\text{-}CN)]$ and $[\{Pt(bzq)(C_6F_5)(CN)\}Tl(THF)]$ are shown in Figure 1a-b. The photophysical properties of all compounds were studied in powder, polymer films, and solution states. While the precursors and diplatinum complexes display in rigid media, structured emissions ascribed to typical mixed $^3LC/^3MLCT$ excited states, the heteronuclear Pt-Tl compounds, exhibit unstructured strong emissions associated to the formation of mettallophillic Pt-Tl bonds. Furthermore, the Pt-Tl compounds show in solid state reversible vapochromic and vapoluminiscent response to some organic solvent such as MeOH and mechanochromic behavior by simple grinding. As an example, the solvatochromic behavior of $[\{Pt(bzq)(C_6F_5)(CN)\}Tl(THF)]$ is given in Figure 1c.

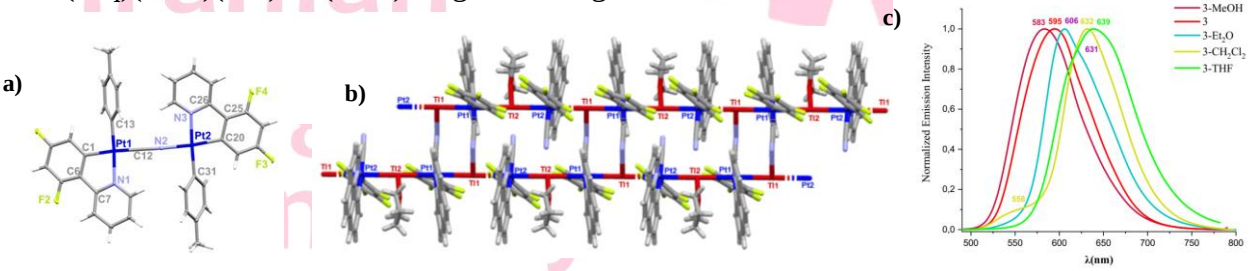


Figure 1. a) View of the molecular structure of **$(NBu_4)[Pt_2(dfppy)_2(p\text{-}MeC_6H_4)_2(\mu\text{-}CN)]$,** b) **$[\{Pt(bzq)(C_6F_5)(CN)\}\text{-}Tl(THF)]_n$,** c) Normalized emission spectra of the orange solid **$[\{Pt(bzq)(C_6F_5)(CN)\}Tl(THF)]$**, and (**$[\{Pt(bzq)(C_6F_5)(CN)\}Tl(THF)]$-solvent**). ($\lambda_{ex}$ 405, 415nm).

Keywords: CycloPlatinated, metallophillic ineractions, cyanide.

References

[1] J. Forniés, S. Fuertes, A. Martín, V. Sicilia, B. Gilc and E. Lalinde, *Dalton Trans*., **2009**, 2224-2234.
[2] M. Sadeghian, D.G.Segura, M. Golbon Haghighi, N. Safari, E. Lalinde, and M. T. Moreno, *Inorg. Chem*. **2023**, 62, 4, 1513–1529.